

Gas Doping on the Topological Insulator Bi_2Se_3 Surface

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Gas molecule doping on the topological insulator Bi_2Se_3 surface with existing Se vacancies is investigated using first-principles calculations. Consistent with experiments, NO_2 and O_2 are found to occupy the Se vacancy sites, remove vacancy-doped electrons and restore the band structure of a perfect surface. In contrast, NO and H_2 do not favor passivation of such vacancies. Interestingly we have revealed a NO_2 dissociation process that can well explain the speculative introduced “photon-doping” effect reported by recent experiments. Experimental strategies to validate this mechanism are presented. The choice and the effect of different passivators are discussed. This step paves the way for the usage of such materials in device applications utilizing robust topological surface states.

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Three-dimensional (3D) topological insulators (TI) have attracted extensive research interest recently [1–4]. Their novel topological surface states (TSS) in the bulk energy gap open great practical potential in spintronics and quantum computation by realizing the Majorana fermions [5]. However, most TI materials available today are poor insulators in the bulk due to heavy defect doping [3, 4, and references therein], hindering the utilization of the TSS in practice. To remove the bulk carriers, surface doping with gas molecules was adopted as a powerful tool in experiments [6–10], though the underlying detailed atomistic mechanisms are still unknown. Exploring chemical reactions and understanding the modified surface structures are crucial to comprehend the current experimental results and help finding new methods to achieve the bulk insulating state.

As of today, the most attractive TI material is Bi_2Se_3 [6, 11, 12], demonstrating simple Dirac-type TSS along with large bulk energy gap. Presumably due to the Se vacancies, however, it is found to be a n -doped semiconductor. To achieve a real bulk insulator, NO_2 [6, 8, 10] and O_2 [7, 9] gas species were used to dope the surface and successively remove the donated bulk conduction electrons. In particular, the NO_2 doped Bi_2Se_3 surface exhibits a mysterious behavior, in which the surface loses electrons when exposed to photon flux in angle-resolved photoemission spectroscopy (ARPES) experiments [6, 8]. This is very different from the cases of graphene [13] and another known TI material Bi_2Te_3 [8, 14], where the surface gains electrons back through desorbing NO_2 by the photon exposure. Though this photon-assisted stimulation or the so-called “photon-doping” method was employed to manipulate the surface bands in experiments [15], the underlying mechanism remains to be defined. In this letter, we have studied from first-principles the reaction of gas molecules on the Bi_2Se_3 surface containing Se vacancies and conclude how these affect the TSS.

The first-principles molecular dynamic (FPMD) simu-

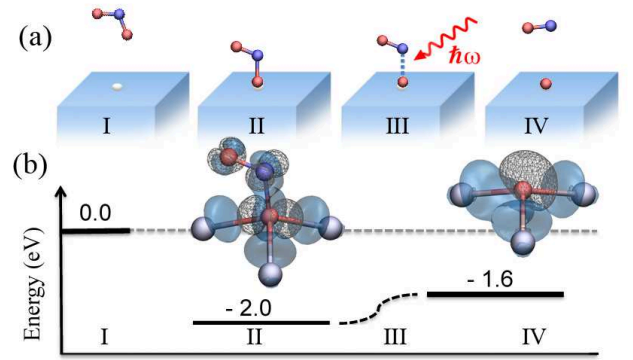


FIG. 1. (a) Schematic of NO_2 molecule adsorption and dissociation processes and (b) corresponding reaction energetics on the Bi_2Se_3 surface with a Se vacancy. The Se vacancy is indicated by the white dot (step I) and donates two electrons that can dope the surface. During NO_2 exposure, the molecule occupies the vacancy site quickly with one O binding to three Bi atoms from the second atomic layer (step II). The corresponding N-O bond become weaker compared to before adsorption (step I). The stable adsorption structure is shown in (b) together with charge density difference before and after adsorption. The donor electrons transfer partially from the vacancy to NO_2 . Under external photon exposure (step III), the weakened N-O bond breaks, resulting in the NO_2 dissociation into $\text{NO} + \text{O}$ (step IV). The NO molecule leaves the surface, while O passivates the vacancy. In this case, two donor electrons transfer to the O atom and the vacancy is compensated. White balls stand for Bi atoms, red for O, and blue for N. In the isovalue surface plots of the charge difference, solid blue (wired gray) color denotes charge depletion (gain).

lation was employed to investigate the dynamic process of chemical adsorption and search for the stable atomic configurations. In bulk Bi_2Se_3 , five atomic layers form a quintuple layer (QL) while the coupling between two such QLs is of the van der Waals type [11]. Here we used a two-QL-thick slab model containing 3×3 primitive unit cells in the xy plane to simulate a surface for

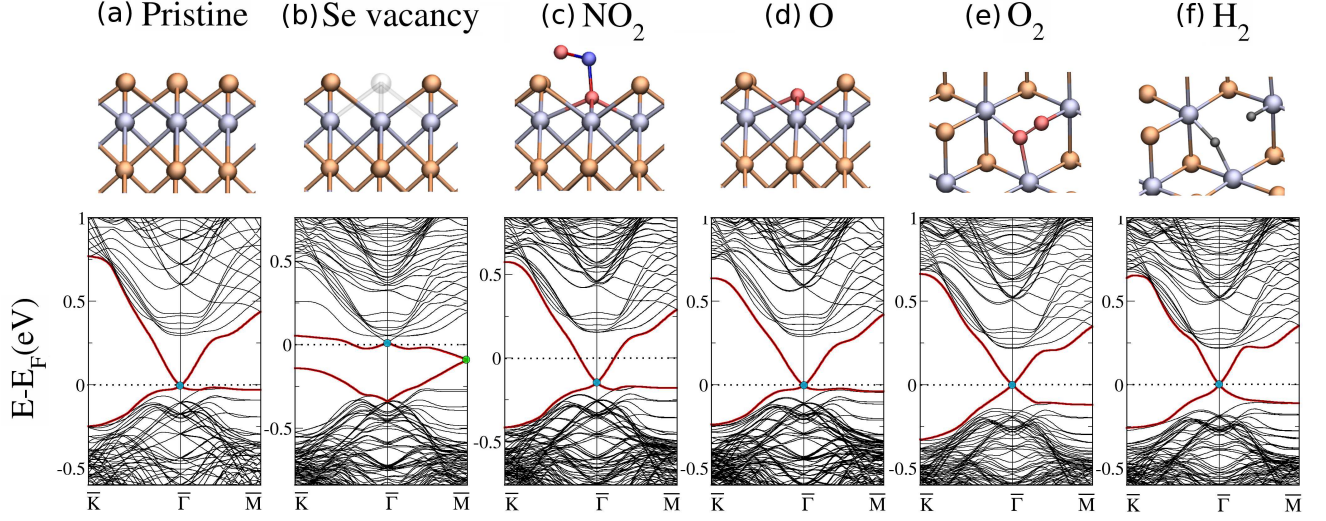


FIG. 2. Atomic structures and band structures for (a) a perfect Bi_2Se_3 surface, (b) a surface with a Se vacancy, (c) NO_2 adsorption, (d) O adsorption from the dissociated NO_2 , (e) O_2 and (f) H_2 adsorption. Bands are aligned to their valence band maximum at $\bar{\Gamma}$. The Fermi energy is shifted to zero. (a)-(d) show structures from side view, whereas (e)-(f) from the top view. Red lines indicate the surface states. White balls stand for Bi, yellow for Se, red for O, blue for N and small gray for H atoms. The transparent ball indicate the missing Se at the vacancy in (b). Band structures are calculated from a 3×3 supercell of seven QLs thick. Colored circles denote Dirac points.

the FPMD adsorption studies. Thicker slabs were tested to yield correct and converged results. Both the pristine surface and the surface with a Se vacancy at the outmost layer were considered for adsorption of NO_2 , NO , O_2 and H_2 molecules. FPMD calculations including van der Waals interactions [16] have been performed at 300 K in microcanonical ensemble (NVE) with an integration time-step of 1.0 fs [17]. We let the calculations run for 5.0 ps, while in worst case, roughly after 1.5 ps no more significant structural changes were observed. Using the optimized structures from FPMD, the slab was extended to seven QLs thick to prevent the interactions between states from the top and the bottom surfaces [18, 19]. Inversion symmetry was maintained by placing the same molecules on both surfaces. Subsequently, band structure calculations were carried out to investigate the electronic properties.[20]

The results are shown in Fig. 2. The pristine surface has a single pair of Dirac-like TSS with the Fermi level E_F crossing the Dirac point at $\bar{\Gamma}$, consistent with previous calculations [11]. When a Se vacancy forms on the surface, E_F shifts to the bulk conduction band bottom, resulting in n -type doping as observed in experiments. Interestingly, the surface states are energetically changed considerably by the existing vacancies. The original Dirac point at $\bar{\Gamma}$ shifts upward and almost merges into the conduction band, while a new Dirac point forms at the \bar{M} point (Fig. 2(b)). In the bulk gap, E_F still intersects the TSS odd times, indicating the topological nontrivial character. It should be noted that in our model Se vacancies distribute periodically on the surface,

reflecting the employed supercell periodic boundary condition. However due to the vacancy random distribution on the real sample surfaces, the ARPES measured only a single Dirac point at $\bar{\Gamma}$ in the primitive Brillouin zone [6, 12, 14]. This illustrates a possible way to engineer the Dirac point by designing well-ordered surface potential.

NO_2 and NO . In the FPMD simulations, NO_2 molecules are placed above both the pristine surface and the surface with vacancy. NO_2 moves freely above the pristine surface whereby no strong binding effect is observed. The total energy calculation reveals that NO_2 physisorbs on this surface with a weak adsorption potential energy (APE) of - 0.4 eV, resulting in tiny charge transfer from the surface to the molecule. However, on the defected surface NO_2 chemisorbed at the vacancy site quickly. One of the NO_2 oxygens, labeled as O1, adsorbs and binds to three Bi atoms from the second atomic layer, see Fig. 1(a) step II. The equilibrium bond length of N-O1 is elongated to 1.6 Å compared to the other N-O bond of 1.3 Å, indicating weakened N-O1 bond upon adsorption. Proceeding further, different FPMD replicas resulted into two situations. Firstly, in the majority of the simulations, stable adsorption of NO_2 at the vacancy with the APE of - 2.0 eV took place. The corresponding band structure is depicted in Fig. 2(c), whereby the Dirac cone is recovered at $\bar{\Gamma}$. However, the surface is yet slightly electron-doped with E_F 0.15 eV above the Dirac point. This indicates that NO_2 can not take away all donor electrons from the vacancy. In the other situation, localized vibrations cause the weakened N-O1 bond to break. Subsequently,

NO_2 dissociates into NO which leaves the surface, while the O1 atom passivates the vacancy. The respective APE decreases to -1.6 eV. To estimate the dissociation energy barrier, we performed density-functional calculations using the nudged elastic band method [21] and monitor dissociation to happen smoothly at a barrier of about 0.4 eV. From the related band structure in Fig. 2(d), we see the O1 atom passivation shifts E_F further down to the Dirac point and totally restores the band structure of the pristine surface. This can be understood by the fact that the single O1 atom can accommodate all two extra electrons from the Se vacancy, more than NO_2 in the former case, as illustrated by the charge density change in Fig. 1(b). Contrary to NO_2 , NO binds weakly (APE of -0.6 eV) and does not yield a similar good passivation of the vacancy, due to its much lower electron affinity.

It is interesting to compare these results with recent ARPES measurements [6, 15]. In experiments, the Fermi level is 0.3 eV above the Dirac point. Supposing all doped electrons are due to the Se vacancies, a dosage of 0.1 Langmuir(L) of NO_2 can shift E_F down by 0.15 eV. After dosing with NO_2 , in experiment two additional non-dispersive peaks appear at the binding energies of -4.0 eV and -7.5 eV [6]. This agrees with our calculated density of states (DOS) projected onto NO_2 (Fig. 3(b)), where partial DOS analysis (not shown here) indicates that the peak at ~ -4.0 eV is mainly due to both O atoms and the other at ~ -7.5 eV due to all N and O atoms. The ARPES results are found to remain stable with temperature varying from 10 K to 300 K. This can be explained by the large APE and the dissociation barrier (0.4 eV), much too high to be overcome by RT thermal fluctuations. Thereby NO_2 will neither desorb nor dissociate at 300 K. Moreover, the surface with a dose of 0.1 L can also be further hole-doped by extensive photon (energy 28-55 eV) exposure until E_F reaches the Dirac point [15], called as “photon-doping”. Considering that NO_2 molecules dissociate into $\text{NO} + \text{O}$ under laser pulse irradiation [22], the above experimental observation may be explained by the NO_2 dissociation process (Fig. 1 step III). High-energy photons stimulate the N-O1 bond to break and subsequently transfer remaining electrons from the vacancy to the O1 atom, finally downshifting E_F to the Dirac point. We conclude that a dosage of 0.1 L of NO_2 passivates most of the Se vacancies on the surface, as the experimental E_F position (0.15 eV above the Dirac point) is the same as our calculated one, see Fig. 2(c). Therefore photon exposure induces an O-passivated surface without extra donor electrons. In addition, without photon exposure a dosage of 2.0 L more can also shift E_F down to the Dirac point. This can be attributed to the weak adsorption of NO_2 on the pristine surface, see above, where much less electron transfer happens compared to that of the strong adsorption on the vacancy.

The proposed dissociation mechanism can be easily checked in experiments. One way is to monitor whether

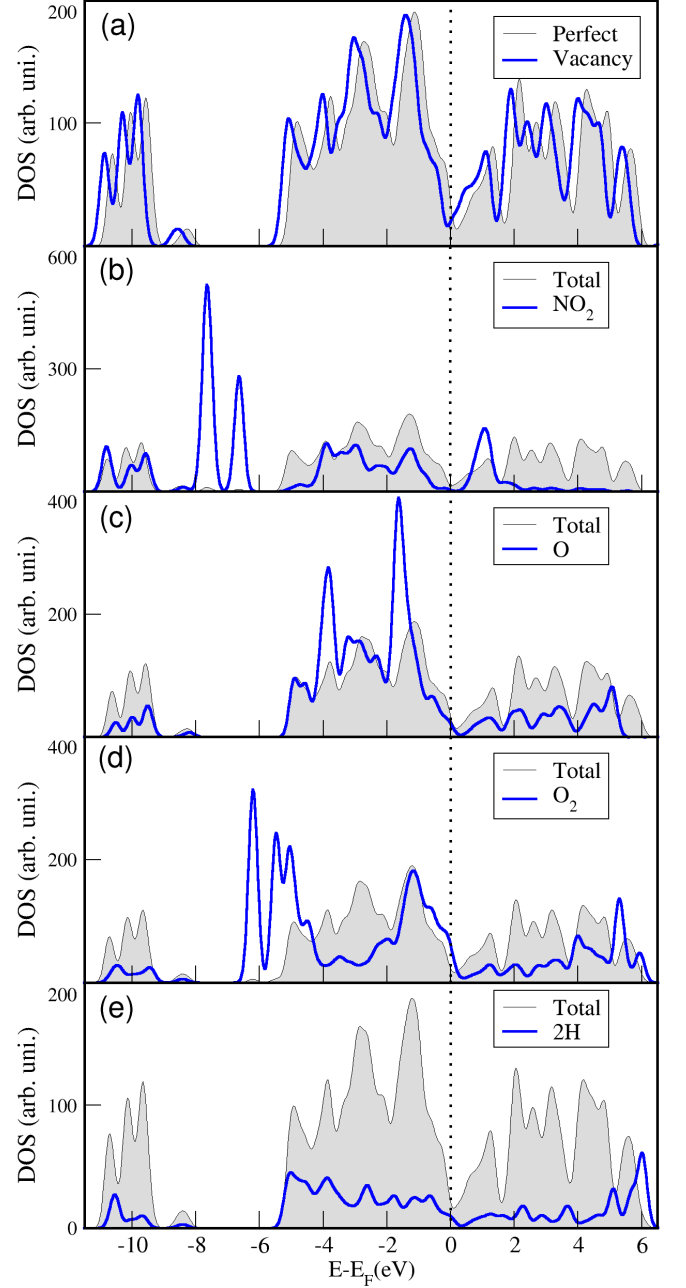


FIG. 3. Density of states (DOS) for (a) the perfect pristine surface and the one with a Se vacancy, (b) NO_2 , (c) a single O atom, (d) O_2 , and (e) H_2 passivated. To be more clear the adsorbates PDOS have been scales by N_X/N_{Tot} , where N_X is the number of atoms in the adsorbate and N_{Tot} is the total number of atoms in the supercell.

the composition of NO (NO_2) increases (decreases) after photon exposure. The second way is to measure the valence band spectra. We predicted that the peak at ~ -7.5 eV will become weaker or even disappear after extensive photon exposure, as indicated by the projected DOS in Fig. 3(c). The third alternative is to see the surface using STM or from vibration spectra. Additionally,

one can find that the monoatomic oxygen, which is generally used in semiconductor industry for plasma ashing, can be an excellent passivator to Se vacancies, if under controllable exposure.

O₂ and H₂. The O₂ molecule also gets adsorbed in the vacancy site quickly with an estimated APE of - 3.4 eV. The two O atoms still remain connected to each other with one O (labeled as O1) binding to one Bi atom and the other O (O2) binding to the other two Bi atoms, as Fig. 2(e) shows. In the equilibrium structure, the O1-Bi bond length is ~ 2.2 Å, while two O2-Bi bonds form at ~ 2.4 Å. Concluding from the band structure analysis, O₂ captures two extra electrons from the vacancy and recover the neutral-charged TSS very well. After adsorption no O₂ dissociation was observed in any of our MD simulations, clearly due to stiffness of O=O bond. This suggests why photon exposure had not any improving effect in experiments with O₂ [7, 9]. In contrast, H₂ does not occupy the vacancy site in the MD adsorption simulations. However after artificially saturating dangling bonds with hydrogens, the relaxed structure shows similar bondings with three below Bi atoms as in the O₂ case, see Fig. 2(f). This passivation can also restore a perfect Dirac-type band structure (Fig. 2(f)). Though H₂ adsorption is not favored in dynamics, single H atoms can be an ideal passivation to Bi dangling bonds in theoretical studies, removing nontrivial surface dangling bond states and simplify the physics underlying.

In summary, we have studied the chemical adsorption of gas molecules (NO₂, NO, O₂ and H₂) on the Bi₂Se₃ surface. The passivation of common Se surface vacancies is found to gain the donor electrons much more effectively than weak adsorption on the pristine surface. The local atomic structures after adsorption are revealed and the band structures are compared. NO₂ is observed to passivate the vacancy and accommodate partially the vacancy-doped electrons. By overcoming a moderate energy barrier (*e.g.* with laser stimulation), NO₂ dissociates into NO and a single O atom, whereby the latter occupies the vacancy and accommodates all donor electrons. This dissociation and charge transfer can explain the mysterious “photon-doping” effect seen in ARPES experiments. As well, both O₂ molecule and the single O atom are found to passivate the vacancy very well and restore the surface band structure to the charge neutral state. In contrast, NO and H₂ are not favorable adsorbates on the Bi₂Se₃ surface. The combination of MD with electronic structure analysis is shown to be versatile in explaining experimental observations along with suggesting new routes for device engineering, by tailoring different dopants and TI materials.

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